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Assessment of bisphenol-A in the urban water cycle

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Abstract

The plasticizer bisphenol-A (BPA) is common to municipal wastewaters and can exert toxicity to exposed organisms in the environment. Here BPA concentration at 5 sewage treatment works (STW) and distribution throughout a river catchment in South West UK were investigated. Sampling sites included influent and effluent wastewater (n=5), river water (n=7) and digested sludge (n=2) which were monitored for 7 consecutive days. Findings revealed average BPA loads in influent wastewater at two STWs were 10-37 times greater than the other wastewaters monitored. Concentrations up to ~100 µg L⁻¹ were measured considerably higher than previously reported for municipal wastewaters. Temporal variability throughout the week (i.e., highest concentrations during weekdays) suggests these high concentration are linked with industrial activity. Despite ≥90 % removal during wastewater treatment, notable concentrations remained in tested effluent (62-892 ng L⁻¹). However, minimal impact on BPA concentrations in river water was observed for any of the effluents. The maximum BPA concentration found in river water was 117 ng L⁻¹ which is considerably lower than the current predicted no effect concentration of 1.6 µg L⁻¹. Nevertheless, analysis of digested sludge from sites which received these elevated BPA levels revealed average concentrations of 4.6±0.3 and 38.7±5.4 µg g⁻¹. These sludge BPA concentrations are considerably greater than previously reported and are attributed to the high BPA loading in influent wastewater. A typical sludge application regime to agricultural land would result in a predicted BPA concentration of 297 ng g⁻¹ in soil. Further studies are needed on the toxicological thresholds of exposed terrestrial organisms in amended soils to better assess the environmental risk here.

Keywords: bisphenol-A; plasticizer; wastewater; river; sludge; industry

1. Introduction

It is estimated that 2.2 million tonnes of bisphenol-A (BPA) is manufactured globally each year (Kelland, 2010), and demand is expected to rise by 6-7 % per year (Wright-Walters et al., 2011). BPA is used in the production of epoxy resins and polycarbonate plastics as well as phenol resins, polyacrylates and polyesters (Staples et al., 1998). Due to its high production and widespread usage in numerous products, BPA is commonly found in the environment, including surface waters (Belfroid et al., 2002; Santhi et al., 2012), despite a relatively short environmental half-life of 2.5 to 5 days (Babić et al., 2016). Concentrations previously reported in river water are generally in the ng L^{-1} range (Belfroid et al., 2002; Santhi et al., 2012; Petrie et al., 2015). However, concentrations exceeding $1 \mu\text{g L}^{-1}$ have been reported including river waters in the United States, Japan, Spain, China and the Netherlands (Matsumoto et al., 1982; Staples et al., 2000; Belfroid et al., 2002; Vethaak et al., 2005; Céspedes et al., 2005). The presence of BPA in the aquatic environment is concerning due to its possible toxic effects on exposed biota (Brian et al., 2005). Evidence of endocrine disruption caused by BPA has been observed in numerous aquatic organisms including fish, amphibians and invertebrate (Kang et al., 2008). These toxicity studies conducted under laboratory conditions typically use BPA at $\mu\text{g L}^{-1}$ concentration levels. Risk assessment of BPA has established a predicted no effect concentration (PNEC) of $1.6 \mu\text{g L}^{-1}$ established (EU, 2008). However, this PNEC has been questioned by the scientific community with the suggestion that such levels may not be adequate to protect the most sensitive organisms to BPA exposure (Oehlmann et al., 2008).

The main source of BPA in rivers is from the discharge of wastewater effluents. There are other possible sources such as the leaching of BPA from submerged or discarded plastic in the river itself. Nevertheless, BPA is present in municipal wastewaters at high concentration due to the continual leaching from plastics and resins (Rubin, 2011; Flint et al., 2012), including pipes and drinking cups and bottles. Typical concentrations of BPA in municipal wastewater influent are $<5 \mu\text{g L}^{-1}$ (Rudel et al., 1998; Lee and Peart, 2000; Zafra et al., 2003; Hernando et al., 2004; Drewes et al., 2005; Petrie et al., 2015). However it can also be present in municipal wastewater from the discharge of industrial wastewater. Manufacturing and processing industries can be permitted to discharge their waste into municipal wastewater systems for treatment. Industrial wastewater from a paper production facility has previously been found to contain BPA concentrations ranging from 28 to $72 \mu\text{g L}^{-1}$ (Fürhaker et al., 2000).

BPA is considered moderately biodegradable during biological wastewater treatment with removal transformation $>80\%$ commonly reported (Clara et al., 2005; Petrie et al., 2015). Nevertheless BPA is commonly reported in treated effluents discharged into the environment (Nakada et al., 2006; Gardner et al., 2012; Petrie et al., 2015).

Other than being biodegradable BPA is considered moderately hydrophobic and has a Log K_{OW} of 3.4 (Staples et al., 1998). Therefore it can adsorb to particulate organic matter including sludge during biological wastewater treatment. BPA has been reported from ng g^{-1} levels to $>300 \mu\text{g g}^{-1}$ in activated sludge (Meesters and Schröder, 2002; Nie et al., 2009). Excess or waste activated sludge produced is normally digested anaerobically. Organic contaminants such as BPA have been found to persist during anaerobic digestion with concentrations up to $1 \mu\text{g g}^{-1}$ reported (Tan et al., 2007; Pothitou and Voutsas, 2008; Stasinakis et al., 2008; Nie et al., 2009; Langdon et al., 2011; Guerra et al., 2015). Persisting BPA can be a significant issue as digested sludge (or biosolids) are recycled to land as fertilizer. Staples et al (2010) investigated the possible risks of BPA exposure to organisms at the base of terrestrial food webs (2 species of invertebrates and 6 plant species). A soil PNEC of $3.7 \mu\text{g g}^{-1}$ was proposed indicating the risk to these organisms is low based on current BPA concentrations reported in sludge for land application. However, a lowest observed effect concentration of $10 \mu\text{g g}^{-1}$ has been reported for female juvenile woodlouse (Lemos et al., 2010). Applying an assessment factor of 10 would result in a soil PNEC of $1 \mu\text{g g}^{-1}$. There are comparatively fewer studies which investigate BPA toxicity to exposed organisms in the terrestrial environment which make the derivation of a PNEC challenging.

Due to the continuing increase in BPA production and use, it is essential to understand its current distribution in the water cycle. Such information is vital for assessing environmental risk and developing environmental policy. Therefore the aim of this study was to provide a holistic

understanding of the source, fate and behaviour of BPA throughout a river catchment. To achieve this understanding the following objectives were identified: (i) to investigate the presence and source of BPA in influent wastewaters, (ii) to determine the fate and behaviour of BPA during wastewater treatment, (iii) to assess the impact of effluent discharges to river water quality with respect to BPA, and (iv) to evaluate the significance of BPA in digested sludge destined for land application. This was achieved by investigating BPA at 5 strategic sampling sites throughout a river catchment in South West UK. At each site, influent and effluent wastewater, and river water from upstream and downstream of the effluent discharge point (where possible) were sampled for 7 consecutive days. Digested sludge was also collected from sites with sludge treatment facilities.

2. Materials and methods

2.1. Materials

The analytical reference standards BPA and BPA-d16 were purchased from Sigma-Aldrich (Gillingham, UK). Methanol (MeOH) was HPLC grade and obtained from Sigma-Aldrich. Water used throughout the study was 18.2 MΩ quality (Elga, Marlow, UK). Ammonium fluoride (NH₄F) for the preparation of mobile phases was obtained from Fisher Scientific (Loughborough, UK). Oasis® HLB and MCX (60 mg, 3 mL) SPE cartridges were purchased from Waters (Manchester, UK).

2.2. Extraction methods

Aqueous matrices (influent wastewater – 50 mL, effluent wastewater – 50 mL and river waters – 100 mL) were filtered using GF/F filters (0.7 µm) and adjusted to pH 7.5 ±0.1. Samples were then spiked with 50 ng (50 µL of a 1 µg mL⁻¹ methanolic solution) of BPA-d16 and loaded onto Oasis® HLB cartridges conditioned using 2 mL MeOH followed by 2 mL H₂O at 1 mL min⁻¹. Samples were loaded at 5 mL min⁻¹ and dried under vacuum. Elution was performed using 4 mL MeOH at a rate of 1 mL min⁻¹. Methanolic extracts were subsequently dried under nitrogen using a TurboVap evaporator (Caliper, UK, 40 °C, N₂, <5 psi). Dried extracts were reconstituted in 500 µL 80:20 H₂O:MeOH ready for analysis.

Suspended particulate matter from influent wastewaters and digested sludge were frozen, freeze-dried and 0.25 g samples spiked with 50 ng of BPA-d16. Samples were then left for a minimum of 1 h. Extraction was achieved using 25 mL of 50:50 MeOH:H₂O (pH 2) at 110 °C using a 800 W MARS 6 microwave (CEM, UK). Samples extracts were adjusted to <5 % MeOH using H₂O (pH 2). SPE was performed using Oasis® MCX cartridges conditioned with 2 mL MeOH followed by 2 mL H₂O (pH 2). Samples were loaded and dried as described previously. Elution was performed using 2 mL 0.6 % HCOOH in MeOH. Once dried extracts were reconstituted in 500 µL 80:20 H₂O:MeOH and filtered using pre-LCMS 0.2 µm PTFE filters (Whatman, Puradisc). The full methodology is described in Petrie et al (2016).

2.3. UPLC-MS/MS analysis

Chromatography was performed on a Waters Acquity UPLC system (Waters, Manchester, UK). A reversed-phase BEH C18 column (150 x 1.0 mm, 1.7 µm particle size) (Waters, Manchester, UK) was utilised with a 0.2 µm, 2.1 mm in-line column filter maintained at 25 °C. Separation was achieved using 80:20 H₂O:MeOH containing 1 mM NH₄F (mobile phase A) and 5:95 H₂O:MeOH also containing 1 mM NH₄F (mobile phase B). Starting conditions were 100 % A which was maintained for 0.5 min. This was reduced to 40 % A over 2 min and to 0 % A over a further 5.5 min. These conditions were maintained for 6 min before returning to starting conditions. Starting conditions were held for 8.4 min to allow re-equilibration (total run time was 22.5 min). The mobile phase flow rate was 0.04 mL min⁻¹ and the injection volume was 15 µL. The UPLC was coupled to a Xevo TQD Triple Quadrupole Mass Spectrometer (Waters, Manchester, UK), equipped with an electrospray ionisation source. Analysis was performed in negative ionisation mode with a capillary voltage of 3.20 kV. The source temperature

was 150 °C and the desolvation temperature was 400 °C. The cone gas flow was 100 L h⁻¹ and the desolvation gas flow was 550 L h⁻¹. Nitrogen was used as the nebulising and desolvation gas, and argon as the collision gas. The multiple reaction monitoring (MRM) transitions for BPA were 227.3>212.1 m/z (quantifier, 22 eV collision energy) and 227.3>132.7 m/z (qualifier, 25 eV collision energy). The MRM transition for BPA-d16 was 241.1>223.1 m/z (20 eV collision energy). The cone voltage for both BPA and BPA-d16 was 40 V.

2.4. Quality control

Spiked quality control samples (as well as procedural blanks) were analysed every 7 environmental samples to ensure the quality of generated data. Samples used to determine recovery were spiked at additional concentration levels of 100 and 1,000 ng L⁻¹ for wastewaters and 50 and 500 ng L⁻¹ for river waters. Solid matrices were spiked at 100 and 1,000 ng g⁻¹. Methods recoveries were in the range 64-112 % for influent wastewater, 109-120 % for effluent wastewater, 89-131 % for river waters and 55-96 % for influent wastewater particulate matter and digested sludge. Furthermore, standard tolerances of deviation in retention time and ion ratio were adhered to (Official Journal of the European Communities, 2002). Method detection limits (MDLs) and method quantitation limits (MQLs) for liquid samples were <1 ng L⁻¹ and <3 ng L⁻¹, respectively (Petrie et al., 2016). In digested sludge the MDL was 0.3 ng g⁻¹ and the MQL was 0.9 ng g⁻¹. All sample analysis was performed in duplicate with the average of the 2 analysis reported.

2.5. Sampling regime

The studied river catchment is located in the South West of the UK and covers an area of approximately 2,000 km² (Figure 1). The population within the catchment is ~1.5 million. Sampling was undertaken at five STWs (named STWs A-E), utilising a range of treatment technologies (Table 1). Trickling filters (STW B, C and D), conventional activated sludge (STW A) and sequencing batch reactors (STW E) were all investigated. At each site influent wastewater (between screening and primary sedimentation) and effluent wastewater was collected. Digested sludge was also collected at those sites which had anaerobic digestion facilities (Site B and E). River water was collected from upstream and downstream of the effluent discharge point at varying distances depending on accessibility (Table 1). River water was not collected for Site E as the STW discharges directly to estuarine waters.

Wastewater was collected as volume proportional 24 h composites with average sub-sample collection frequencies of ≤15 min. Sub-samples (80 mL) were cooled to 4 °C during collection to limit biological activity and pooled after 24 h (Petrie et al., 2017). River waters (8 L) were collected as grab samples. All samples were transported to the laboratory on ice for further processing. Grab samples of digested sludge were also collected. At each site sampling was undertaken for 7 consecutive days running from Wednesday to Tuesday with no significant rainfall experienced. Sampling was undertaken during summer in 2015.

BPA removal efficiency during wastewater treatment was calculated according to:

$$\text{Removal (\%)} = \frac{(\text{Influent} - \text{Effluent})}{\text{Influent}} \times 100 \quad [1]$$

Influent is the BPA influent wastewater load (g d⁻¹) and *Effluent* is the BPA effluent wastewater load (g d⁻¹).

3. Results and discussion

3.1. BPA in municipal wastewaters and its source

BPA loads normalized accounting for wastewater flow and population/inhabitant numbers ($\text{mg } 1000^{-1} \text{ inh. d}^{-1}$) were used to compare BPA levels in influent wastewater at 5 different STWs. Findings revealed considerable spatial variability in BPA load. STWs A, C and D were similar, with loads ($n=7$) in the range 201 to $339 \text{ mg } 1000^{-1} \text{ inh. d}^{-1}$ (Figure 2). However, average loads at STWs B and E were $3,400 \pm 2,820$ and $7,420 \pm 6,280 \text{ mg } 1000^{-1} \text{ inh. d}^{-1}$, respectively, more than an order of magnitude greater than A, C and D. These elevated levels corresponded to influent concentrations up to $100 \mu\text{g L}^{-1}$ and are considerably greater than previously observed municipal wastewaters in the UK (Petrie et al., 2015). BPA is typically found in municipal wastewater at concentrations in the range 500-2,000 ng L^{-1} (Clara et al., 2005; Nakada et al., 2006; Fernandez et al., 2007; Gatidou et al., 2007; Guerra et al., 2015; Petrie et al., 2015). Such concentrations are considered typical for household wastewater due to BPA leaching from polycarbonates and epoxy resins (Rubin, 2011; Flint et al., 2012), including pipes and other items such as water bottles. At STW B and E where elevated BPA loads were observed, both have $\geq 5\%$ industrial wastewater contributions within their upstream wastewater network (Table 1). In contrast STW A, C and D received $\leq 1\%$ industrial contributions to the total wastewater flow.

Another notable difference between the BPA loads observed in the studied municipal wastewaters was the temporal variability over the 7 d study period. At STWs A, C and D the variability in load (expressed as RSD) was in the range 12 to 38 % (Figure 2). This stability showed BPA loads here were relatively consistent, supporting the hypothesis that it is continually leached from plastics and resins in the upstream wastewater network. Variability in BPA load to STW B and E was 83 % and 85 %, respectively. The comparatively high variability at STW B and E was due to marked differences in BPA loads observed between weekdays and weekends. For example, at STW E weekday (Monday to Friday) loads ranged from 3,210 to $19,100 \text{ mg } 1000^{-1} \text{ inh. d}^{-1}$ (Figure 2). On Saturday and Sunday loads were considerably lower at 1,530 and $1,500 \text{ mg } 1000^{-1} \text{ inh. d}^{-1}$, respectively. Similarly, weekday loads up to $7,060 \text{ mg } 1000^{-1} \text{ inh. d}^{-1}$ were found at STW B whereas weekend loads were 538-539 $\text{mg } 1000^{-1} \text{ inh. d}^{-1}$. This difference suggests the high loads of BPA observed at STW B and E was attributed to industrial wastewater discharges. These elevated loads are most likely from manufacturing industries which use BPA in the production process, explaining the considerably lower loads during weekends. Such a relationship has not been observed previously for BPA in municipal wastewaters.

Currently, businesses which produce wastewater (also known as ‘trade effluents’) through manufacturing or processing of materials require consent to discharge into public sewers. Water utilities issue a permit stating the volume of wastewater which can be discharged as well as the limits of certain pollutants which the business must adhere to. Permits do not limit non-regulated chemicals such as BPA, but can be used to identify the types of business discharging industrial wastewater into the sewer network. Therefore, these permits can be used to indicate the possible source of the elevated BPA levels found. At STW B, a total of 14 permits are issued with the majority being food manufacture, car washing and launderette facilities, and these discharges are not expected to account for the high BPA loads observed. However, one permit gives the trader description as ‘rubber to metal bonding’. In such industries, BPA can be used in the manufacture process (Green and Mowrey, 2001; Khoudary et al., 2012), and this facility is the most likely source of the high loads observed. At STW E, a total of 145 permits are issued from a range of industries making the identification of the likely source(s) of the high BPA loads here more difficult. Possible sources identified from the permit information include ‘leachate from landfill/industrial landfill’, ‘manufacture of corrugated/polystyrene packaging’ and ‘printing and coating packing materials’.

3.2. Fate and behaviour of BPA in wastewater and during wastewater treatment

BPA has been found to be stable in influent wastewaters stored at 18°C for 24 h (Petrie et al., 2017). Although this does not replicate conditions experienced in sewers, the lack of degradation suggests BPA loads are largely unchanged when they arrive at the STW because the upstream sewer hydraulic retention times (HRTs) were ≤ 24 h (Table 1). In influent wastewaters up to 18 % of the BPA load was found in the particulate phase of wastewater. This partitioning is mainly attributed to its log K_{ow} of

3.40 which makes it susceptible to sorption onto particulate organic matter (Staples et al., 1998). Calculated BPA particulate-aqueous phase partition distribution coefficients ($\log K_d$) ranged from 2.9 to 3.0 at STWs A, C and E. At STWs B and D $\log K_d$'s were notably lower ($\log K_d$ 2.6) (Table 2). This difference was due to BPA being distributed at higher concentrations in the aqueous phase relative to the particulate phase of influent wastewaters. These findings are in agreement with work by pH can also influence BPA sorption to organic matter (Clara et al., 2004); however, the pH of influent wastewater was similar between STWs (7.53-7.77) and probably did not contribute to the differences in $\log K_d$ observed.

Mean removals of BPA during wastewater treatment ranged from 91 to 98 % (n=7) (Table 2). Removals by different process type were 98 ± 1 % by the SBRs (STW E), 91 ± 6 % by conventional activated sludge (STW B) and 95 ± 5 %, 92 ± 2 % and 94 ± 2 % by the trickling filters (STWs A, C and D, respectively). These removals are typical of what is reported in the literature for secondary biological STWs (e.g., trickling filters and activated sludge) with removals of >80 % typical (Clara et al., 2005; Drewes et al., 2005; Nakada et al., 2006). Removal here is mainly attributed to biological degradation and sorption to particulate matter (Staples et al., 1998; Zhao et al., 2008; Stasinakis et al., 2013). Notable partitioning of BPA in both primary and secondary sludge has been reported previously, with $\log K_d$ of 3.2 and 2.9, respectively (Stasinakis et al., 2013). Mean BPA concentrations in effluents at STWs A, C and D were 37 ± 19 , 63 ± 37 and 94 ± 24 ng L⁻¹, respectively (Table 2). To better understand the possible environmental risk it is preferred to report concentration over normalized load. Over the course of the 7 day monitoring period no substantial changes in BPA concentration were noted (Figure 3).

There were no notable differences between observed BPA removal at STWs B and E compared to STWs A, C and D. Despite high removal efficiency during wastewater treatment (>90 %), comparatively high concentrations remained in treated effluent. Effluent concentrations at STWs B and E were 474 ± 277 and 462 ± 266 ng L⁻¹ (Table 2). Furthermore, the temporal trends in influent wastewater were translated to effluent observations with highest concentrations found during weekdays (Figure 3). The highest concentration recorded was 892 ng L⁻¹ at STW B on Monday. Considering the STW HRT of 24.5 h (STW B, Table 1), industrial discharges of BPA from Monday should be observed in effluent on Tuesday. However, 24 h composite samples were collected from this STW at 10:30 am. Therefore any BPA discharged into the sewer network at approximately 6:00 am on Monday morning will be collected as part of the Monday effluent sample.

3.3. BPA in the receiving river and the impact of effluent discharges

To assess the impact of effluent discharge to river water quality, spot samples from both upstream and downstream of the effluent discharge point were collected over 7 consecutive days. Downstream samples were collected at a minimum of 0.5 km below the effluent discharge point (Table 1). STW A is the furthest up the river catchment and is in a rural location. BPA was not detected (<1 ng L⁻¹) in any river water sample collected upstream of the effluent discharge point of STW A. As there was no suitable access points to the river downstream of STW A (i.e., within adequate proximity to the effluent discharge point), concentrations here were estimated using upstream and effluent BPA loads, as well as river flow data (e.g., $\text{Downstream BPA conc.} = \frac{\text{Upstream BPA load} + \text{effluent BPA load}}{\text{River flow}}$). This equation assumes instantaneous mixing of river water and effluent without any loss of BPA. Assuming a zero loss of BPA is unlikely due to the relatively short half-life of BPA in river waters (Kang and Kondo, 2002), and this estimation is therefore conservative towards the BPA concentration. The estimated downstream BPA concentrations at STW A ranged from 1.9 to 16.2 ng L⁻¹ (Figure 4).

BPA concentrations upstream of STW B ranged from 20.1 to 38.1 ng L⁻¹ (average = 30.1 ± 6.6 ng L⁻¹) (Figure 4). Downstream BPA concentrations ranged from 15.2 to 57.6 ng L⁻¹ (average = 38.1 ± 16.3 ng L⁻¹). There was no substantial impact to the receiving river here despite the higher BPA concentrations in wastewater effluent due to industrial inputs. We suspect that there was little impact due to an effluent/riverine dilution factor of 15 (Table 1). However, it should be noted that STWs can have

considerably lower dilution factor or effectively no dilution in some cases (Gardner et al., 2013). In such cases the effluent discharge will have a greater impact to river water quality.

Similar findings were observed in river waters collected upstream and downstream of STW C and D effluent discharge points (Figure 4). No river water was collected for STW E as effluent is discharged directly into estuarine waters. The highest riverine concentration reported was 116.9 ng L⁻¹ upstream of STW D on Monday. On 2 days, upstream river water samples were found to contain higher concentrations of BPA than the downstream sample. Short-term temporal concentration variability which was not accounted for using spot sampling could be responsible for this observation. Nevertheless, the BPA concentrations reported in river waters are similar to those previously reported in the UK (Petrie et al., 2015; Wilkinson et al., 2017) and throughout Europe (Loos et al., 2009).

To assess the possible impact of BPA in the environment we can compare measured river concentrations with the PNEC. All riverine (and effluent) BPA concentrations are below the current PNEC of 1.6 µg L⁻¹ (EU, 2008), and no risk can be assumed. However, the derivation of this PNEC does not include organisms such as mollusks which can be more sensitive to BPA exposure. A review of the literature found the lowest reported EC₁₀ (effective concentration at 10 %) is 14.8 ng L⁻¹, Oehlmann et al. (2006) who investigated the effect of BPA to egg production of the freshwater snail *Marisa cornuarietis*. Applying an action factor of 10 to this value would result in a PNEC of 1.48 ng L⁻¹. At 7 of the 8 river sampling points this proposed PNEC was exceeded indicating a potential risk to the survival of sensitive organisms.

3.4. BPA concentrations in digested sludge and the possible impact on the terrestrial environment

The other main entry route of BPA into the environment is through the application of digested sludge and biosolids to agricultural land. Within the catchment area studied, 2 STWs process sludge for biogas production (STW B and E). Both receive sludge from other STWs but the majority treated is produced on-site. BPA concentrations in digested sludge were 4,560±333 and 38,700±5,410 ng g⁻¹ at STW B and E, respectively (Table 2). Average concentrations previously reported in the literature are typically <1,000 ng g⁻¹ (Tan et al., 2007; Pothitou and Voutsas, 2008; Stasinakis et al., 2008; Nie et al., 2009; Langdon et al., 2011; Guerra et al., 2015). Both digested sludges analysed were obtained from the STWs which receive industrial BPA discharges, explaining the comparatively high concentrations of BPA compared to that previously reported in the literature. Digested sludge from STW E was >8 times higher than sludge from STW B. Elevated concentrations at STW E are attributed to the higher receiving load of BPA than at STW B (Figure 2), and the difference in processing (activated sludge vs. trickling filters). Partitioning into sludge can be considerable for micropollutants during active sludge treatment (Clara et al., 2011; Salgado et al., 2012), and excess (waste) activated sludge is blended with carbon rich primary sludge for digestion. This blending is likely to contribute to the higher BPA concentrations found in digested sludge collected from STW E (Table 2). The trickling filters produce comparatively less sludge (from sloughing of the biofilm) during secondary treatment.

The main concern for the presence of micropollutants such as BPA being present in digested sludge is the land application of sludge to farmland as fertilizer, and the possible impact on the terrestrial environment. Considering a typical sludge application regime as outlined by Stasinakis et al (2008) whereby sludge is applied to soil (1.3 kg L⁻¹) at 10 t ha⁻¹ and tilled to 10 cm would result in an effective dilution factor of 130. Application of sludge from STW E would see a theoretical BPA concentration in soil of 297 ng g⁻¹. However, tilling to a greater depth would result in greater 'dilution', or not conducted at all resulting in higher soil surface BPA concentrations. Controlled laboratory soil degradation studies have found BPA to have a half-life of <3 d (Fent et al., 2003), and concluded that if BPA reaches the terrestrial environment it is not anticipated to be bioavailable. However, the impact of BPA on the terrestrial environment will be dependent on the concentration at which adverse effects are observed. For example if the concentration threshold is very low, even a short half-life can result in BPA concentrations above the critical level for sufficient time for chronic exposure. PNEC has yet

to be established due to insufficient toxicity data available for a full range of terrestrial organisms (Thomaidi et al., 2016).

3.5. Future viewpoint for BPA in municipal wastewaters

BPA entering municipal wastewater has the potential to cause adverse effects to organisms in both riverine and terrestrial environments. To better assess the potential risk, it is essential to have robust toxicological data available for the most sensitive species such that PNECs can be derived for both impacted environments. Despite substantial research on aquatic organisms, uncertainty remains on currently derived PNECs (Oehlmann et al., 2008). This derivation process is likely to take considerable time particularly for terrestrial environments due to the paucity of toxicological information. In the short term it is recommended that improved control of industrial charges containing BPA could be implemented to reduce BPA concentrations in both treated effluents and digested sludge. For example, UK businesses which discharge wastewater into municipal streams are currently required to apply for a wastewater discharge permit. Such permits outline limits for legislated pollutants (e.g., metals) but do not include emerging micropollutants such as BPA. Inclusion of micropollutants such as BPA in wastewater discharge permits would oblige companies to put steps in place to reduce their BPA emissions to municipal wastewater. Pretreatment or process reduction would help reduce the elevated levels of BPA found in effluent and treated sludge due to industrial discharges (Figure 3; Table 3). In the longer term, end-of-pipe treatment options may need to be considered once PNECs are established.

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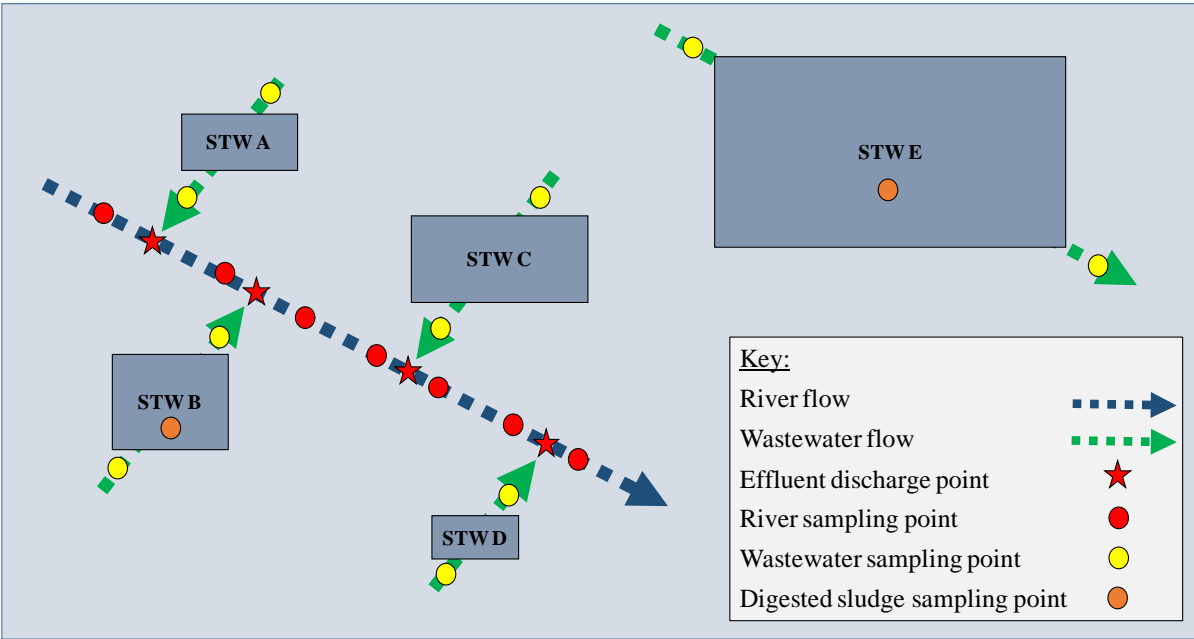


Figure 1. Catchment area schematic illustrating sampling points

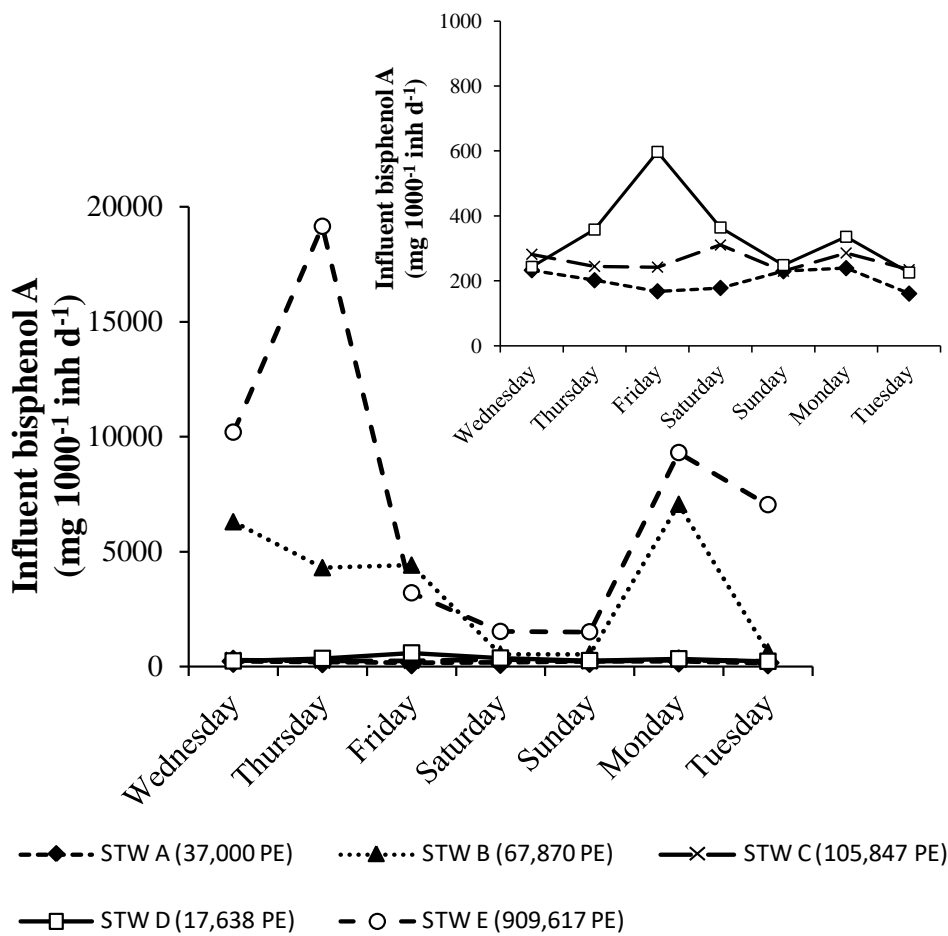


Figure 2. Temporal change in BPA influent wastewater load (mg 1000⁻¹ inh. d⁻¹) during 7 d at five STWs in South West UK (n=2). Inset, BPA loads at STWs A, C and D only. Note: load includes both aqueous and particulate phase of wastewater. Key: STW, sewage treatment works; PE, population equivalents

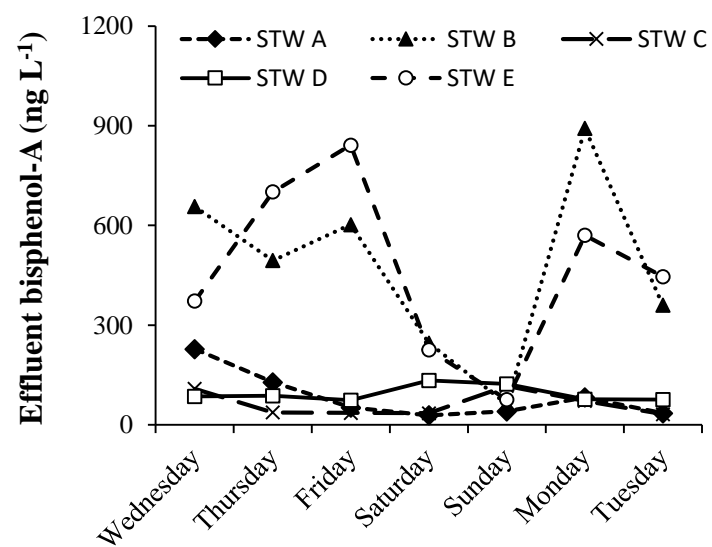


Figure 3. BPA concentrations in effluent wastewater from five different STWs during 7 d (n=2). Key: STW, sewage treatment works

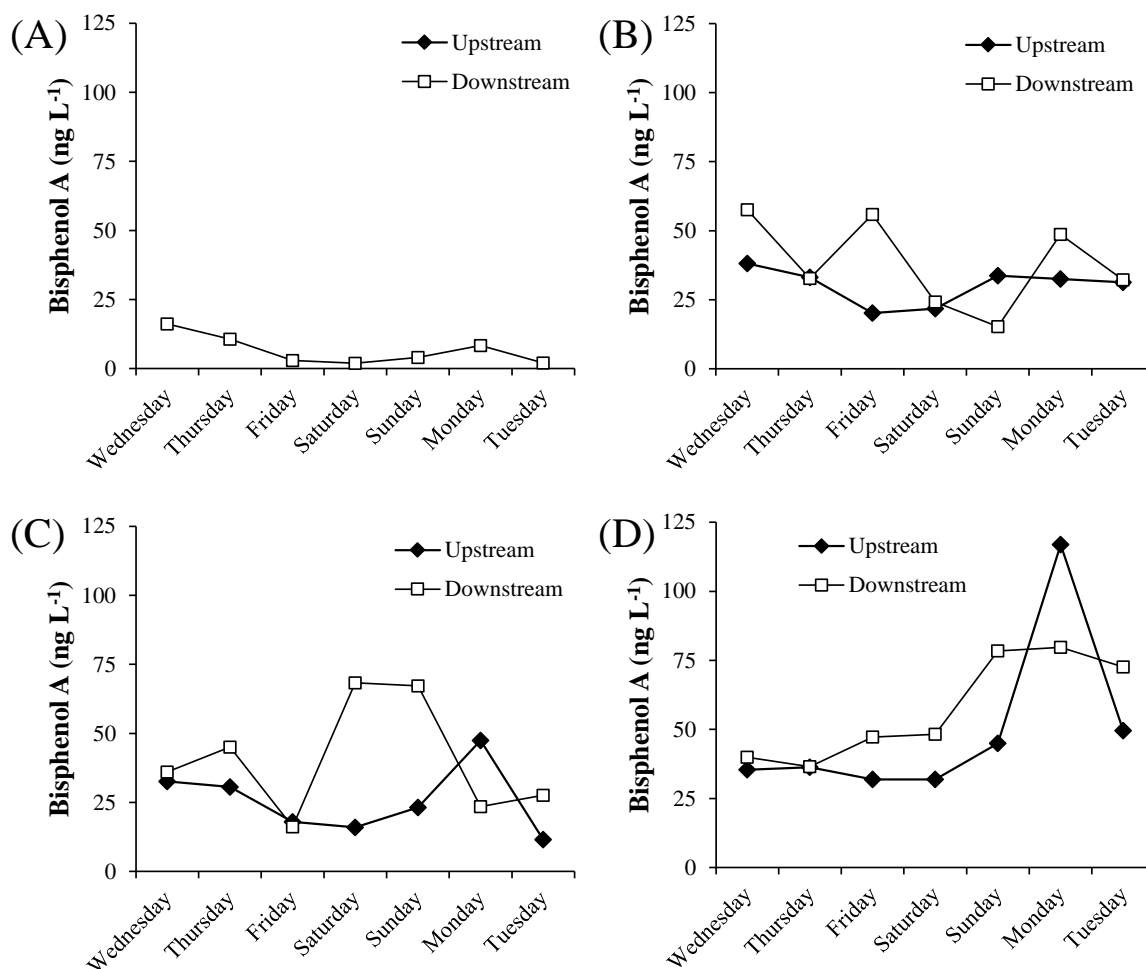


Figure 4. Riverine concentrations of BPA from spot samples collected upstream and downstream of effluent discharge points from STW A (A), STW B (B), STW C (C) and STW D (D) (n=2). Note: BPA in upstream river water at STW A was $<1 \text{ ng L}^{-1}$, and BPA reported in downstream river water was estimated using effluent and upstream river data. Key: STW, sewage treatment works; PNEC, predicted no effect concentration

Table 1. Site information of studied STWs and corresponding river locations

Site	Sewer residence time ^a (h)	STW secondary process ^b	SRT (d)	HRT ^a (h)	Media type	Configuration	Population served (no. of inhabitants)	Industrial contribution (%)	Mean flow (m ³ d ⁻¹)	Effluent dilution factor	River sampling, distance to discharge point (km)	
											Upstream	Downstream
A	<0.5-4	AS	19	46.2	-	Carbonaceous & nitrifying	37,000	<1	8,242±3,085	14	0.5	n/a ^c
B	<0.5-4	TF	n/a	24.5	Stone	Carbonaceous & nitrifying	67,870	19	11,202±3,202	15	0.5	0.5
C	<0.5-9	TF	n/a	13.9	Stone – limestone	Carbonaceous & nitrifying	105,847	1	24,875±2,167	15	2	2
D	<0.5-2	TF	n/a	17.6	Stone – blast furnace slag	Carbonaceous & nitrifying	17,638	<1	2,924±199	113	1	1
E	<1-24	90 % SBR 10 % AS	4 8	10.9 25.8	-	Carbonaceous	909,617	5	153,061±12,245	n/a ^d	-	-

Key: STW, wastewater treatment process; SRT, solids retention time; HRT, hydraulic retention time; AS, activated sludge; TF, trickling filter; SBR, sequencing batch reactor

^aUnder summer (dry weather) flow

^bAll STWs utilised primary sedimentation dosed with ferric sulfate for phosphorus removal and all processes used conventional sedimentation following secondary treatment except SBRs which decanted following settling *in-situ*

^cDue to limited river access, mass loads in river water downstream of the discharge point were estimated by adding effluent loads with upstream river water loads. This assumes complete mixing without any BPA losses. BPA concentrations in downstream river water were then estimated using river flow data.

^dEffluent discharged into estuary

Table 2. Concentrations of BPA observed in wastewater matrices during 7 d sampling and their removal efficiency during wastewater treatment (average from n=7 days)

STW	Influent wastewater (ng L ⁻¹)	Influent wastewater (ng g ⁻¹)	Influent wastewater log K _d	Removal from aqueous phase (%)	Effluent wastewater (ng L ⁻¹)	Digested sludge (ng g ⁻¹)
A	874±266	754±187	2.9	91±6	37±19	-
B	20,400±17,000	8,090±6,320	2.6	95±5	474±277	4,560±333
C	976±105	794±307	2.9	92±2	63±37	-
D	1,660±240	1,850±3,130	3.0	94±2	94±24	-
E	37,200±31,700	16,300±17,500	2.6	98±1	462±266	38,700±5,410

Key: STW, wastewater treatment works